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Planar laser-induced fluorescence imaging of Si and SiO during pulsed laser ablation of Si

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ABSTRACT

Planar laser induced fluorescence has been used to acquire time sequence images of ground-state, neutral Si and SiO during laser ablation of an Si target in vacuum and in the presence of a background gas at a fluence of 3–4 J/cm². The SiO images, taken in air, strongly suggest that the observed SiO is created through reaction of silicon with oxygen at the contact front as the plume expands.

1 INTRODUCTION

Pulsed laser deposition (PLD) in the presence of oxygen is an attractive method to deposit oxide films such as YBa₂Cu₃O_{7- δ} (YBCO), VO₂,¹ Cu₂O,² CuO,² ZnO,³ PZT,³ SiO₂,^{4,5} and GeO₂.⁶ However, the factors governing oxide film growth are still very poorly understood, due largely to the complexity of this process. Some of the important features of PLD with a background gas are the absorption of laser energy by the target and by electrons in the plasma above the target, the supersonic expansion of the hot plasma particles into the background gas, chemistry within the plume or between plume species and background molecules, and finally the impact of plume species, shock-heated background gas molecules, and reactive intermediates created by gas-phase chemistry with the substrate.

Time-resolved imaging of the plume can shed light on some of these complex processes. Ideally, one would like to acquire temporally- and spatially-resolved images of individual chemical species in their electronic ground states, since these provide the greatest insight into the chemistry and are most directly comparable to numerical simulations.

Several different methods have been employed to image PLD plumes, including emission,⁷ dye laser absorp-

tion,⁸ shadow photography,^{9,10} and laser-induced fluorescence.^{11,12} (For an excellent recent review of these methods, see Geohegan.¹³) Of these, only laser-induced fluorescence (LIF) provides truly spatially-resolved images; the other techniques result in line-of-sight averages. LIF has the additional advantage (like absorption spectroscopy) that it is species-specific, and can be used to quantitatively measure neutral ground-state populations, which are non-luminous and therefore not seen by emission methods.

Single-point (non-imaging) LIF has been used in several studies to acquire time-of-flight distributions of ground-state ablated target species.^{14–20} One-dimensional line images using LIF have also been reported by the group at Kyushu University.^{21–23} There are apparently only two reports of two-dimensional planar LIF (PLIF) imaging of a laser-ablation plume.^{11,12}

The vast majority of the diagnostics work on PLD plumes has dealt with ablation of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (YBCO), due to the interest in growing superconducting YBCO films. Among the LIF studies of ablation in the presence of a background gas, all have focused on YBCO ablation in oxygen,^{14,17–19,21–23} with the exception of the two PLIF studies, which examined ZrC ablation into argon¹² and barium ablation into helium.¹¹

Unfortunately, the YBCO system is very complex. Multiple atomic and oxide species are desorbed from the target, and since they differ greatly in molecular weight, segregation in the plume is expected.²⁴ In addition, a large number of chemical intermediates may be formed by gas-phase chemistry, and oxide species formed in this way are difficult to distinguish from oxides desorbed from the target (although it is possible¹⁹).

To begin to understand a process as complex as PLD, it is desirable to start with a simpler system, with an elemental target and restricted gas-phase chemistry. In the present paper, we have chosen to examine ablation of silicon into a background gas (air or argon). We present here PLIF images of ground-state atomic silicon (Si) and ground-state SiO formed due to gas-phase chemistry. The present images of SiO are, to our knowledge, the first reported of a reactive intermediate species generated during pulsed laser deposition.

2 EXPERIMENTAL

The experiments were carried out in a stainless steel vacuum cube with quartz windows. The experimental setup is shown schematically in Figure 2. The target was a silicon wafer and was rotated continuously during the experiments. The ablation laser was an injection-seeded 10 Hz excimer laser running on KrF with a nominal energy per pulse of 175 mJ. The excimer laser beam was focused onto the target at normal incidence using a single 500 mm focal length aberration-corrected doublet lens. The spot size on the target was approximately 2.5 mm diameter, resulting in a fluence of 3 – 4 J/cm².

An excimer-pumped dye laser was used for the fluorescence excitation. Coumarin 480 dye was used for both the Si and SiO measurements, with a nominal energy per pulse of 1 mJ and a bandwidth of 0.15 cm⁻¹.

The dye laser beam was transformed into a collimated sheet nominally 1 cm wide using a telescope made from a -64 mm cylindrical lens and a +500 mm spherical lens. The laser sheet was brought to a soft waist of thickness 0.02 cm.

A gated single-microchannel-plate intensified CCD camera oriented perpendicular to the dye laser sheet and to the target was used to collect the fluorescence. A 105 mm f/4.5 UV-Nikor lens was used to image the fluorescence onto the image intensifier. The gate width was set nominally at 50 ns. The camera was operated in an RS-170 video format and the image recorded using a frame grabber in a 486 computer.

After the experiment, the intensity profile in the dye laser sheet was measured. The maximum intensity variation across the image was less than 40%. Each image was corrected for the laser sheet intensity profile.

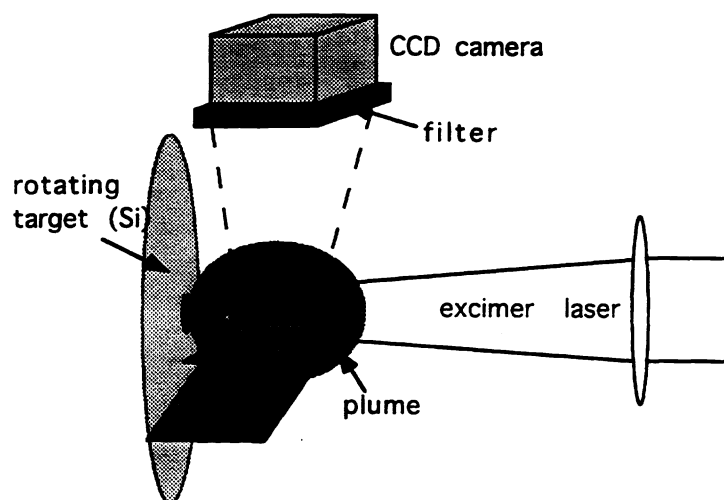


Figure 1: Schematic of experimental setup used for PLIF measurements.

Typically either 20 or 40 images were acquired for each experimental condition and averaged to reduce statistical noise.

2.1 Si detection

For the Si fluorescence experiments, the dye laser output was doubled in BBO to excite the $\text{Si } 3p^2\ ^3P \rightarrow 4s\ ^1P^\circ$ transition near 243.88 nm. While this is a weak transition ($f = 0.002$) the laser energy was sufficient to come within 1/10 of the saturation intensity based on the spontaneous emission rate.

A 290 ± 5 nm bandpass filter was used to collect fluorescence from the $3p^2\ ^1D \leftarrow 4s\ ^1P^\circ$ transition near 288.1 nm. The oscillator strength for this transition is 0.131 and it has a lifetime of 5.5 ns. Since the lifetime is short compared to the expected collisional quenching time, the measured fluorescence intensity is directly proportional to the number density in the $\text{Si } 3p^2\ ^3P$ state.

2.2 SiO detection

For the SiO fluorescence experiments, the dye laser was doubled in BBO to excite an overlap of the $Q1(35)$ and $R1(42)$ transitions in the $\text{SiO } A^1\Pi \leftarrow X^1\Sigma^+(0,0)$ system near 235.25 nm ($f_{00} = 0.13$). These rotational lines were selected since they gave the largest fluorescence signal levels. For an equilibrium rotational population, a peak signal corresponding to these levels would suggest an SiO temperature of order 2500 K. The laser peak intensity in the sheet was estimated to be of order 1/5 the saturation intensity based on the spontaneous emission rate. (Note that any collisional quenching events would raise the saturation intensity, putting us further into the linear regime.)

A 260 ± 10 nm filter was used to detect fluorescence from the (0,4) band as well as portions of emission from the (0,3) and (0,5) bands. A 1 mm thick piece of Schott UG1 filter glass was also used to increase the rejection of scattered KrF laser light. The lifetime of the $A^1\Pi$ state is less than 10 ns, thus we again employed a gate width

of 50 ns. As for Si, the short upper-state lifetime makes collisional quenching of the SiO fluorescence negligible; thus, the signal is directly proportional to the number density in the SiO X $^1\Pi^+$ ($v = 0$) state.

For the SiO measurements, significant luminous emission was detected in the 260 ± 10 nm filter bandpass which interfered with the LIF signal. To overcome this, images were acquired with the laser on and with the laser off and subtracted to remove the emission interference. No interfering emission was observed with the 290 ± 5 nm filter used for the Si experiments.

3 RESULTS

3.1 Si Fluorescence Measurements

3.1.1 Ablation into vacuum

A series of experiments was first carried out without a background gas. In this case, some shot-to-shot variation in the plume was observed. This may have been due to slightly overlapping target areas from one pulse to the next, or to a slight resonant ringing of the silicon wafer we observed due to the 10 Hz excimer laser pulse.

Shown in Figure 2 are the neutral Si atom distributions resulting from ablation in vacuum for delay times between the ablation laser and dye laser of up to 4 μ s. In these images, the target is at the top, the ablation laser is incident vertically upward, and the height of image is 0.96 cm. The intensity scale is renormalized in each image; therefore, within one image the shade (white to black) is linearly proportional to the neutral Si density, but the normalization differs from image to image.

At short times, the images show the expected narrow jet leaving the target surface. The neutral Si at the leading edge of the plume is moving significantly in excess of 10^6 cm/s. The origin of these fast neutrals is unclear, but they may be the result of charge-exchange collisions between slow neutrals and fast ions. However, much of the Si is moving more slowly. The region of peak intensity appears to have a velocity of only $1\text{--}2 \times 10^5$ cm/s.

3.1.2 Ablation into air

Images of neutral Si were acquired for expansion into 60, 100, and 200 mTorr of air at delays up to 4.25 μ s. The results for the 100 mTorr case are shown in Figure 3. As expected, the plume is broadened and slowed compared to the images in Figure 2.

It is interesting to contrast these images to *emission* images of PLD plumes at the same pressure and similar fluence.⁷ Emission images typically show a sharp peak in intensity on-axis at the leading edge of the plume (see e.g. Figure 4), even at 100 mTorr. The present LIF results show that this feature is not due to increased ground-state neutral density. It appears likely that the emission peak is due to a high temperature at the leading edge, resulting in population of excited states. This conclusion is supported by modeling studies as well.²⁵

At 100 mTorr, the images show no hint of a blast wave structure. This is not surprising since the blast wave propagates through the background gas ahead of the desorbed plume species.

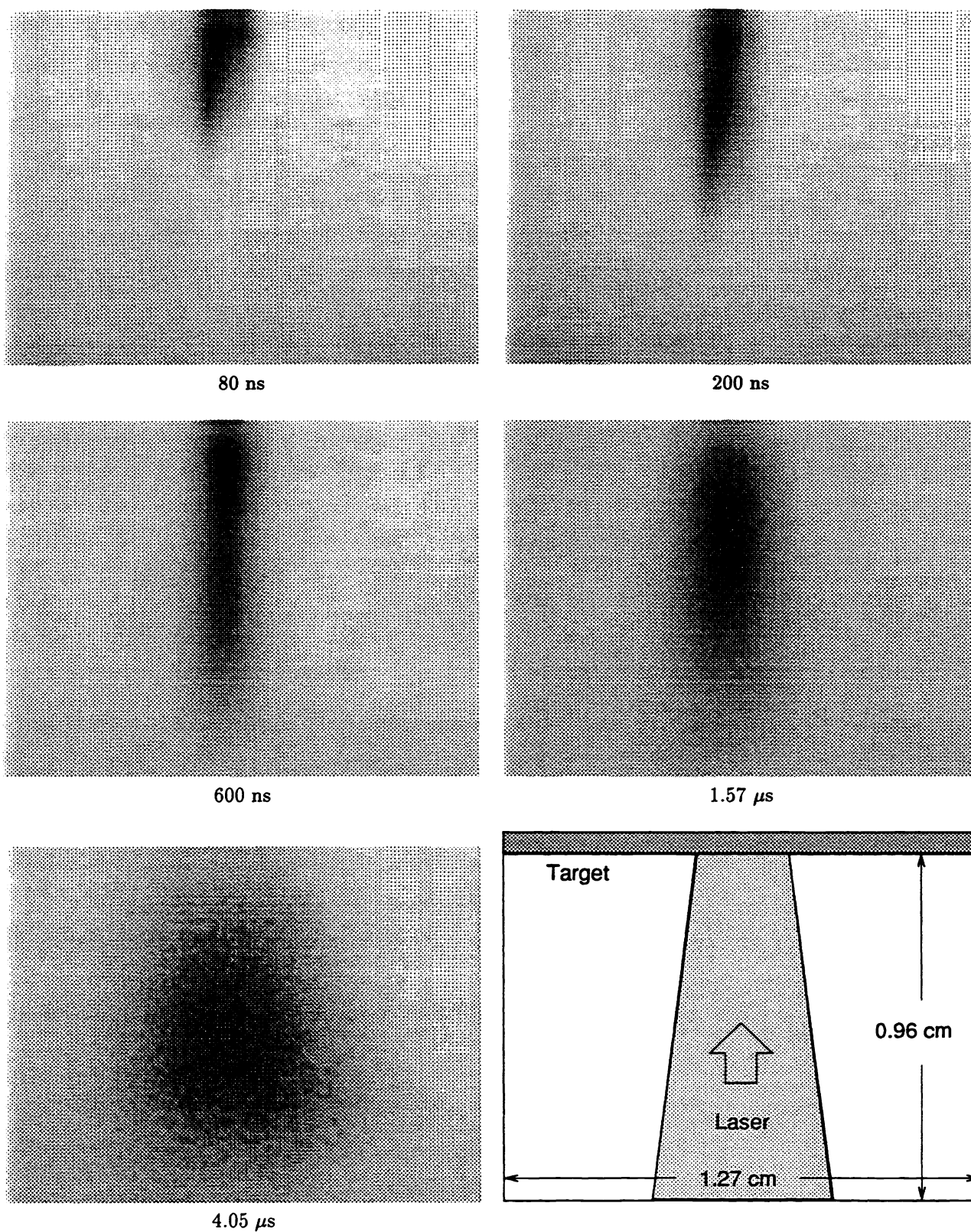
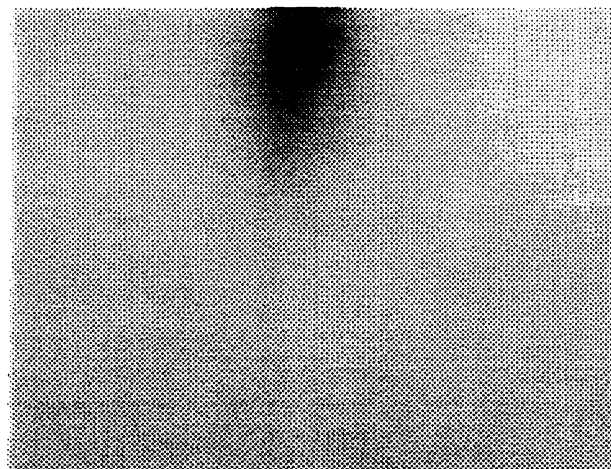
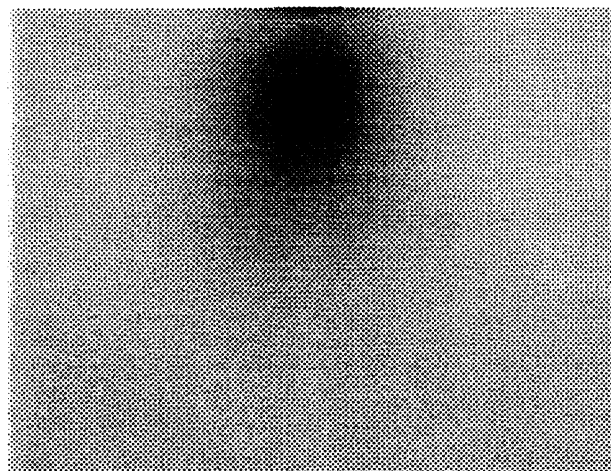


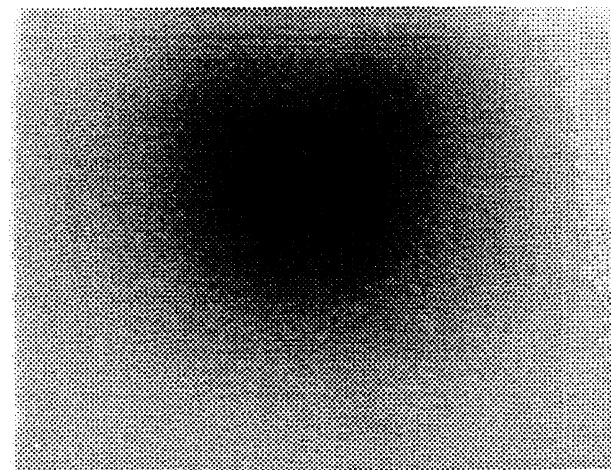
Figure 2: Planar laser-induced fluorescence images of Si expanding into vacuum.



200 ns



1.05 μ s



4.25 μ s

Figure 3: Planar laser-induced fluorescence images of Si expanding into 100 mTorr of air.

3.2 SiO Fluorescence Measurements

Images of ground-state SiO were acquired at a pressure of 1 Torr in air. In contrast to the Si measurements discussed above, in the spectral range used for the SiO fluorescence detection significant interference from emission was observed. The images in Figure 4, acquired in 1 Torr of air, illustrate this. In Figure 4(a), the signal observed without the dye laser at a delay of $2.4 \mu\text{s}$ in the 260 ± 10 filter bandpass with the laser off is shown. This image has the characteristic appearance of an emission image, with the strong peak on-axis near the leading edge of the plume.

The origin of the emission is not known, but is most likely due to excited states of Si. The $\text{Si } 4s^3P^\circ \rightarrow 3p^2^3P$ system consists of 6 strong lines in the region from 251 to 253 nm, which are just within the bandpass of the filter used for SiO detection. The emission signal does not appear to be due to emission from thermally-populated SiO, since it appears also when the background gas is argon (Figure 4(b)), in which case SiO formation should be negligible.

In Figure 4(c), the image is shown for the same conditions but additionally with the dye laser excitation. The primary difference is the ring of SiO laser-induced fluorescence. By subtracting these two images, we obtain the distribution of SiO.

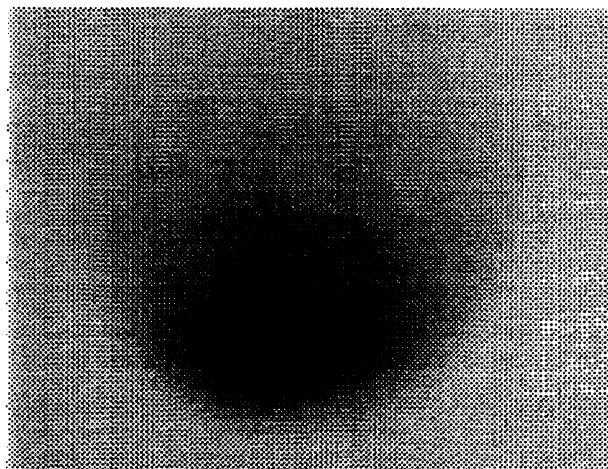
The emission-subtracted SiO distribution obtained for ablation into 1 Torr of air is shown in Figure 5 for delay times of 1, 2, and $3.75 \mu\text{s}$. At $1 \mu\text{s}$, SiO is only observed very near the target. (The dark spot in this image and the "ghost" image of the plume are probably artifacts of the emission-subtraction process.) At 2 and $3.75 \mu\text{s}$, SiO is seen around the entire perimeter of the plume. It is notable that little if any SiO intensity is seen in the center of the plume, in sharp contrast to the Si images. These images strongly suggest that the SiO we observe is created by gas-phase chemistry at the contact front between the Si and air.

The SiO density is observed to be greatest in the wings of the plume near the target. There are several possible explanations for this. It may be that the temperature near the leading edge of the plume is too high for SiO formation. (If the gas were in chemical equilibrium, at 1 Torr little SiO could form for temperatures much above 4000 K.) Alternatively, the observed distribution may simply be the result of the stretching of the interface region as the plume expands. Since the stretching will be greatest on-axis and least near the target, this could account for the observed distribution.

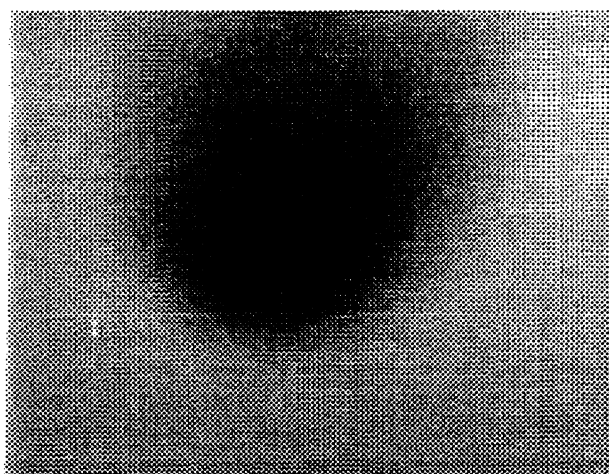
4 SUMMARY

Planar laser-induced fluorescence images have been acquired of ground-state Si and ground-state SiO during laser ablation of Si into vacuum and air at a fluence of $3\text{--}4 \text{ J/cm}^2$. In vacuum, the plume is ejected in a narrow jet, with peak neutral-atom velocities well in excess of 10^6 cm/s . In the presence of 100 mTorr of air, the plume is slower and broader. The images show Si smoothly distributed throughout the plume, and do not show the characteristic forward-peaked intensity seen in emission images. This suggests that these emission features are due to hot excited states, ions, or possibly shock-heated background gas.

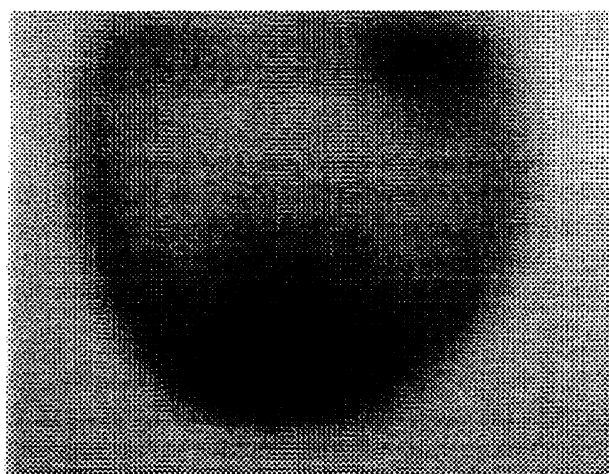
The SiO images show that SiO is localized at the contact front between the ablated Si and the background gas. These images clearly suggest that the observed SiO is produced by gas-phase chemistry, and appear to be the first images of a reactive intermediate produced during reactive pulsed laser ablation.



(a)

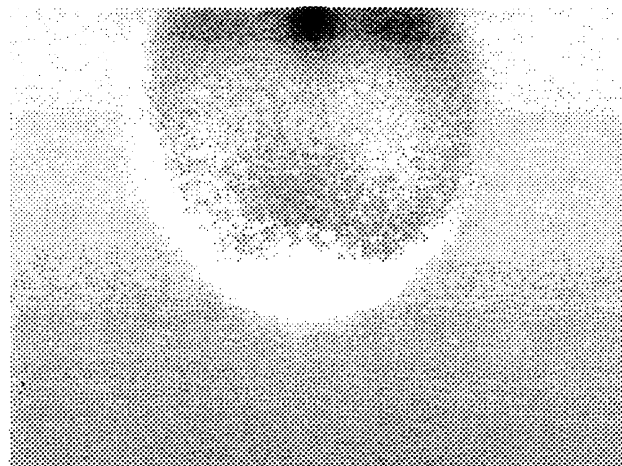


(b)

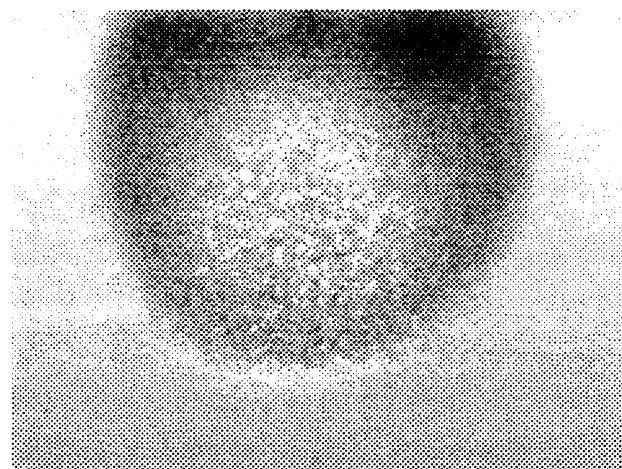


(c)

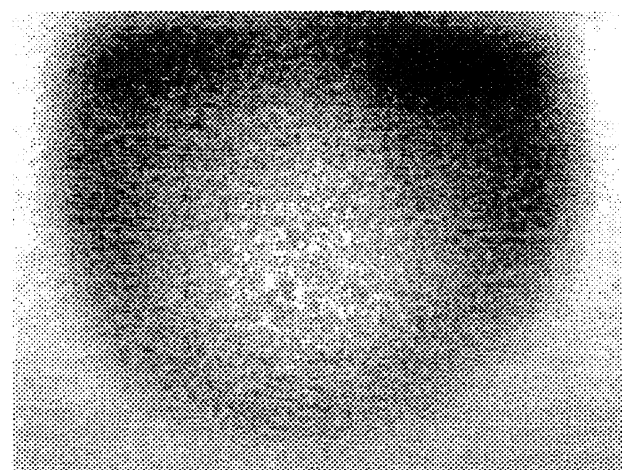
Figure 4: Detection in the 250 – 270 nm spectral range. (a) emission only, 1 Torr air; (b) emission only, 1 Torr argon; (c) emission + SiO LIF, 1 Torr air.



1 μ s



2 μ s



3.75 μ s

Figure 5: Laser-induced fluorescence of SiO with emission subtracted. Background gas is 1 Torr of air.

5 ACKNOWLEDGMENTS

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